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Assembly, crystal structures, and luminescent properties of three new thiocyanate-bridging mercury(II) coordination polymers

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Two ligands, 2-{5,5-dimethyl-3-[2-(pyridin-3-yl)-ethenyl]cyclohex-2-enylidene}propanedinitrile (**L1**) and 2-{5,5-dimethyl-3-[2-(pyridin-2-yl)-ethenyl]cyclohex-2-enylidene}propanedinitrile (**L2**), were synthesized. By reaction of mercury thiocyanate with **L1** and **L2**, respectively, coordination polymers [Hg(**L1**)($\mu_{1,3}$ -SCN)₂]_n (**1**), [Hg(**L1**)₂($\mu_{1,3}$ -SCN)₂]_n (**2**), and [Hg(**L2**)($\mu_{1,3}$ -SCN)(SCN)]_n (**3**) with different structures and topologies were obtained. In **1**, the thiocyanate shows $\mu_{1,3}$ -SCN bridging coordination, and adjacent Hg(II) ions are bridged by two $\mu_{1,3}$ -SCN ions to form an infinite chain with the remaining position of five-coordinate Hg(II) occupied by **L1**. In **2**, the thiocyanate has the same coordination as **1**. However, Hg(II) has octahedral coordination with two **L1** involved in coordination. An unusual feature of **3** is the presence of two types of thiocyanates, one has a S-terminal ligand and the other has a $\mu_{1,3}$ -SCN bridge. The mercury(II) in **3** is four-coordinated by **L2** and three thiocyanates. Luminescent properties and thermal stabilities of **1–3** were studied.

Keywords: Coordination polymer; Mercury(II) thiocyanate; Noncovalent interaction; Crystal structure; Self-assembly

1. Introduction

Self-assembly of organic and inorganic compounds with metal centers is an efficient and widely utilized approach for construction of coordination polymers [1–3]. Synthesis of supramolecular coordination polymers is an active field in coordination chemistry and crystal engineering, because of topologies and fascinating structural diversities, as well as excellent properties [4–6]. A number of supramolecular coordination polymers with specific topologies and applications have been synthesized by assembly of metal salts with ligands. However, there still exists a major challenge in this field because many factors influence the formation of the frameworks and it is difficult to predict the polymeric structures [7].

Anions play key roles in assembly of polymers. In construction of supramolecular polymers, thiocyanate has been used as anion and coligand to bridge metal centers to form polymeric structures. SCN[−] is a linear ambidentate ligand with polarizable π system, and nitrogen and sulfur donors. Thus, it may coordinate to metal ions through terminal or

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bridging modes or both, with potential in building a coordination network [8]. It can adopt different coordinations via nitrogen and sulfur to build coordination networks as well as interlink molecules into frameworks via noncovalent interactions [9]. Many coordination polymers with interesting structures based on thiocyanate have been reported [8–10]. Hg(II) is often employed to construct supramolecular polymers because it may adopt different coordination modes, such as four-, five-, or six-coordination according to the specific structures of the different ligands [11]. When it coordinates with thiocyanate, as a soft acid, it preferentially coordinates by the soft sulfur. Therefore, the Hg(II)–SCN coordination often appears in mercury(II) thiocyanate complexes [11, 12].

In this article, we present the results of our studies on thiocyanate-bridging mercury(II) coordination polymers $[\text{Hg}(\mathbf{L1})(\mu_{1,3}\text{-SCN})_2]_n$ (**1**), $[\text{Hg}(\mathbf{L1})_2(\mu_{1,3}\text{-SCN})_2]_n$ (**2**), and $[\text{Hg}(\mathbf{L2})(\mu_{1,3}\text{-SCN})(\text{SCN})]_n$ (**3**) with different structures and topologies. Bridging $\mu_{1,3}\text{-SCN}$ appears in all the mercury(II) thiocyanate polymers in this work, seldom reported in mercury(II) thiocyanate complexes [12]. The structures are discussed.

2. Experimental

2.1. Materials and physical measurements

All commercially available chemicals are of analytical grade and used without purification. Elemental analyses were carried out on a Perkin-Elmer 240 analyzer. ^1H NMR spectra were recorded on a Bruker AV 400 spectrometer with TMS as internal standard. The mass spectra were obtained on a Micromass GCT-MS spectrometer. IR spectra were recorded from 4000 to 40 cm^{-1} as KBr disks on a Nicolet Nexus 870 spectrophotometer. Solid-state luminescence spectra were measured on a F-4500 FL spectrophotometer. In measurement of emission and excitation spectra, the pass width is 10 nm. Thermal analyses were completed with a Diamond DSC thermal analyzer at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from 25 to $800\text{ }^\circ\text{C}$ in nitrogen.

2.2. Preparation of coordination polymers

A clear methanol solution (10 mL) of $\text{Hg}(\text{SCN})_2$ (0.316 g, 1 mM) was carefully layered onto a solution of **L1** (0.552 g, 2 mM) in dichloromethane (15 mL). The yellow, diamond crystals of **1** and needle crystals of **2** suitable for single-crystal X-ray diffraction were obtained simultaneously by slow interlayer diffusion.

2.2.1. $[\text{Hg}(\mathbf{L1})(\mu_{1,3}\text{-SCN})_2]_n$ (1**).** Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{HgN}_5\text{S}_2$: C, 40.57; H, 2.89; N, 11.83. Found: C, 40.23; H, 2.56; N, 11.61%. IR $\nu(\text{KBr}, \text{cm}^{-1})$: 2221(s, $-\text{C}\equiv\text{N}$), 2120(s, SCN^-), 1571(s), 1529(s), 1423(s), 1394(m), 1311(m), 1293(w), 1213(w), 1186(w), 1159(w), 969(s), 693(s).

2.2.2. $[\text{Hg}(\mathbf{L1})_2(\mu_{1,3}\text{-SCN})_2]_n$ (2**).** Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{HgN}_8\text{S}_2$: C, 52.61; H, 3.95; N, 12.92. Found: C, 52.33; H, 3.61; N, 12.58%. IR $\nu(\text{KBr}, \text{cm}^{-1})$: 2213(s, $-\text{C}\equiv\text{N}$), 2119(s, SCN^-), 1566(s), 1533(s), 1414(s), 1395(m), 1317(m), 1293(w), 1208(w), 1182(w), 1162(w), 972(s), 702(s).

Table 1. Crystal data and structure refinement details for **1–3**.

Compound	1	2	3
Empirical formula	C ₂₀ H ₁₇ HgN ₅ S ₂	C ₃₈ H ₃₄ HgN ₈ S ₂	C ₂₀ H ₁₇ HgN ₅ S ₂
Formula weight	592.10	867.44	592.10
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	21.836(5)	5.836(5)	5.905(5)
<i>b</i> [Å]	5.844(5)	18.104(5)	17.927(5)
<i>c</i> [Å]	18.266(5)	18.104(5)	22.034(5)
α [°]	90.00	73.828(5)	106.479(5)
β [°]	109.733(5)	89.830(5)	97.162(5)
γ [°]	90.00	89.890(5)	99.169(5)
<i>V</i> [Å ³]	2194(2)	1855(2)	2172(2)
<i>Z</i>	4	2	4
<i>T</i> [K]	298(2)	298(2)	298(2)
<i>D</i> Calcd [gcm ⁻³]	1.792	1.553	1.810
μ [mm ⁻¹]	7.220	4.300	7.292
θ range [°]	1.98–26.00	1.16–25.00	0.98–26.00
Total no. data	15,679	13,262	16,505
No. unique data	4281	6455	8251
No. params. refined	255	450	509
<i>R</i> ₁	0.0205	0.0244	0.0288
<i>wR</i> ₂	0.0527	0.0650	0.0762
GOF on <i>F</i> ²	1.026	1.049	1.027

2.2.3. [Hg(L2)($\mu_{1,3}$ -SCN)(SCN)]_n (3**).** The reaction procedure was carried out in similar manner above, except that **L2** (0.552 g, 2 mM) was used instead of **L1**. Yellow, needle crystals of **3** suitable for single-crystal X-ray diffraction were obtained. Yield: 0.38 g (65%) (based on Hg(SCN)₂). Anal. Calcd for C₂₀H₁₇HgN₅S₂: C, 40.57; H, 2.89; N, 11.83. Found: C, 40.98; H, 2.59; N, 12.12%. IR ν (cm⁻¹): 2223(s, -C≡N), 2124(s, SCN⁻), 1568(s), 1533(s), 1533(s), 1468(m), 1435(m), 1256(w), 1115(w), 980(s), 765(s).

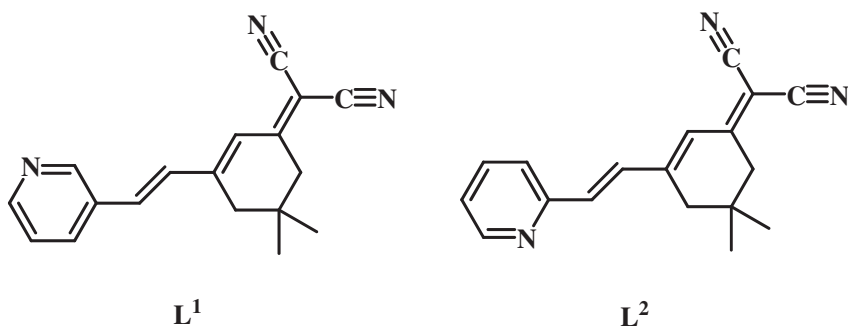
2.3. Crystallographic measurements

X-ray diffraction measurements were performed on a Bruker SMART CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at 298(2) K. Intensity data were collected in the variable ω -scan mode. The structures were solved by direct methods and difference Fourier syntheses. Nonhydrogen atoms were refined anisotropically, and hydrogens were introduced geometrically. Calculations were performed with SHELXTL-97 program package [13]. CCDC 908653 (for **1**), 919425 (for **2**), and 908652 (for **3**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Details of the crystal parameters, data collections, and refinements are listed in table 1, and selected bond distances and angles are given in table S1.

3. Results and discussion

3.1. Syntheses and characterization

The ligands used in construction of our coordination polymers are shown in scheme 1. Details of syntheses of **L1** and **L2** were described in our previous report [14]. The ligands are soluble in common organic solvents such as CH₃OH, CH₂Cl₂, and CHCl₃, facilitating



Scheme 1. The ligands used in the construction of coordination polymers.

solution reaction between the ligands and inorganic salts. Polymers **1–3** were obtained in methanol and dichloromethane mixed solvents by assembly of ligands with $\text{Hg}(\text{SCN})_2$ at room temperature. By addition of $\text{Hg}(\text{SCN})_2$ with **L1** in methanol and dichloromethane, two different crystals, diamond crystals of **1** and needle crystals of **2**, were obtained simultaneously. In preparing the mercury polymers, we carried out reactions of ligands with $\text{Hg}(\text{SCN})_2$ in a 2:1 M ratio. The usual four-coordinate monomer species $\text{Hg}(\text{L1})_2(\text{SCN})_2$ and $\text{Hg}(\text{L2})_2(\text{SCN})_2$ did not form, but produced SCN^- bridged mercury(II) 1-D coordination polymers. The same procedure under similar conditions was carried out several times, and the same result was obtained. In IR spectra of all polymers, the intense $\nu(-\text{C}\equiv\text{N})$ of cyano is easily identified at 2221 (**1**), 2213 (**2**), and 2223 (**3**). The C–N stretch of SCN^- at 2120 (**1**), 2119 (**2**), and 2124 (**3**) cm^{-1} suggests bridging SCN^- [15]. The IR data agree with the results determined by X-ray single-crystal diffraction for **1–3**.

3.2. Description of X-ray crystal structures

3.2.1. $[\text{Hg}(\text{L1})(\mu_{1,3}\text{-SCN})_2]_n$ (1**).** Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic system, space group $P2_1/c$. As shown in figure 1(a), **1** features a 1-D polymeric array $[\text{Hg}(\text{L1})(\mu_{1,3}\text{-SCN})_2]_n$. The asymmetric unit of **1** contains one **L1**, one mercury, and two thiocyanates. The thiocyanates show $\mu_{1,3}\text{-SCN}$ bridging through N and S. Two neighboring mercury(II) centers are bridged by double $\mu_{1,3}\text{-SCN}$ groups to generate an eight-membered $\text{Hg}(\text{SCN})_2\text{Hg}$ unit with $\text{Hg}\cdots\text{Hg}$ distance of 5.844 Å. The $\text{Hg}(\text{SCN})_2\text{Hg}$ units extend to form a 1-D chain along the crystallographic direction [0 1 0]. The S–C–N bond angles of bridging SCN^- are 176.4(3) and 177.8(3)°, and are comparable to those reported [16].

Each $\text{Hg}(\text{II})$ is five-coordinate, bound to one nitrogen of **L1** and four thiocyanates via two $\text{Hg}-\text{S}_{\text{SCN}}$ and two $\text{Hg}-\text{N}_{\text{SCN}}$ bonds. The coordination geometry can be described as a distorted trigonal bipyramid with one N donor from **L1**, two N of two thiocyanates defining the trigonal plane, and the axial positions occupied by two S from the other two thiocyanates [bond angle $\text{S}(3)\text{-Hg-S}(2) = 157.55(4)^\circ$]. The $\text{Hg}-\text{S}2$ and $\text{Hg}-\text{S}3$ bond distances are 2.432(1) and 2.422(1) Å, respectively, within the normal range [17]. The $\text{Hg}-\text{N}$ (1) and $\text{Hg}-\text{N}(4)$ bond distances are 2.399(2) and 2.620(3) Å, respectively, agreeing with the corresponding values [2.23–2.75 Å] for related systems [18–20]. However, the $\text{Hg}-\text{N}(5)$ distance is 2.787(3) Å, slightly longer than the upper limit of 2.75 Å for typical $\text{Hg}-\text{N}$ bond distances [18–20].

The SCN^- also plays a critical role in crystal packing through hydrogen bond interactions. Two neighboring chains are linked through intermolecular hydrogen bond interactions $\text{C}(2)\text{-H}(2)\cdots\text{S}2$ with $\text{H}(2)\cdots\text{S}(2)$ distance of 2.974 Å to generate a 1-D double chain (figure 1(b)). As shown in figure 1(c), the double chains further connect through $\text{C}(7)\text{-H}(7)\cdots\text{S}3$ with $\text{H}(7)\cdots\text{S}(3)$ distance of 2.988 Å to generate a 2-D structure.

3.2.2. $[\text{Hg}(\text{L}1)_2(\mu_{1,3}\text{-SCN})_2]_n$ (2**).** Polymer **2** features a 1-D polymeric arrangement of $[\text{Hg}(\text{L}1)_2(\mu_{1,3}\text{-SCN})_2]_n$ (**2**) (figure 2(a)). The asymmetric unit of **2** contains two crystallographically and conformationally independent units in the asymmetric unit cell, and the two independent units extend to form two parallel 1-D chains, as shown in figure 2(a). In the chains, thiocyanates show $\mu_{1,3}$ -SCN bridging through N and S, and link two neighboring mercury(II) centers. The neighboring $\text{Hg}(1)\cdots\text{Hg}(1)$ and $\text{Hg}(2)\cdots\text{Hg}(2)$ distances are both 5.836 Å. In the $[\text{Hg}(\text{SCN})_2]_n$ chain, all Hg-N and Hg-S bond lengths fall within the reported ranges [17–20]. The thiocyanates are almost linear with a value of the S-C-N bond angles being 178.9(4) and 178.4(5)° (table S1).

Each $\text{Hg}(\text{II})$ lies at a center of symmetry surrounded by six donors. The equatorial positions are occupied by two nitrogens and two sulfurs from four thiocyanates, and two nitrogens of pyridine from two different ligands occupy the axial positions with $\text{Hg}(1)\text{-N}(1)$ and $\text{Hg}(2)\text{-N}(5)$ bond lengths of 2.579(3) and 2.581(3) Å, respectively. Therefore, the polyhedron can be described as a distorted octahedron.

In the crystal structure of **2**, the uncoordinated $\text{-C}\equiv\text{N}$ plays essential roles in generating the 2-D supramolecular structure through $\text{C-H}\cdots\text{N}$ hydrogen bonding interactions. As shown in figure 2(b), the neighboring chains are connected by $\text{C}(11)\text{-H}(11\text{A})\cdots\text{N}(2)$ and C

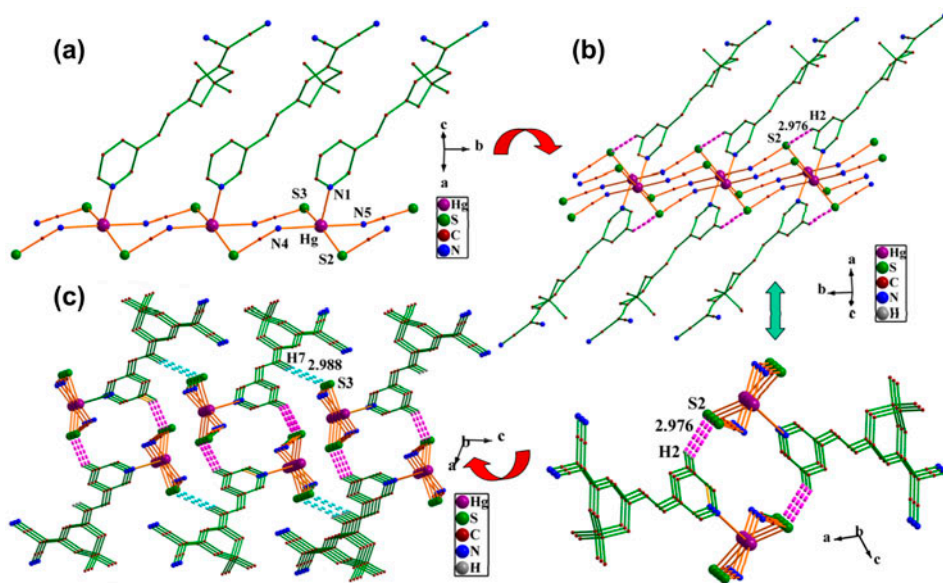


Figure 1. (a) The 1-D structure of **1**. (b) The double 1-D structure of **1** formed by $\text{C-H}\cdots\text{S}$ hydrogen bonds. (c) The 2-D structure of **1** formed by $\text{C-H}\cdots\text{S}$ hydrogen bonding. Dotted lines represent the hydrogen bonding interactions. Hydrogen not participating in hydrogen bonding are omitted for clarity.

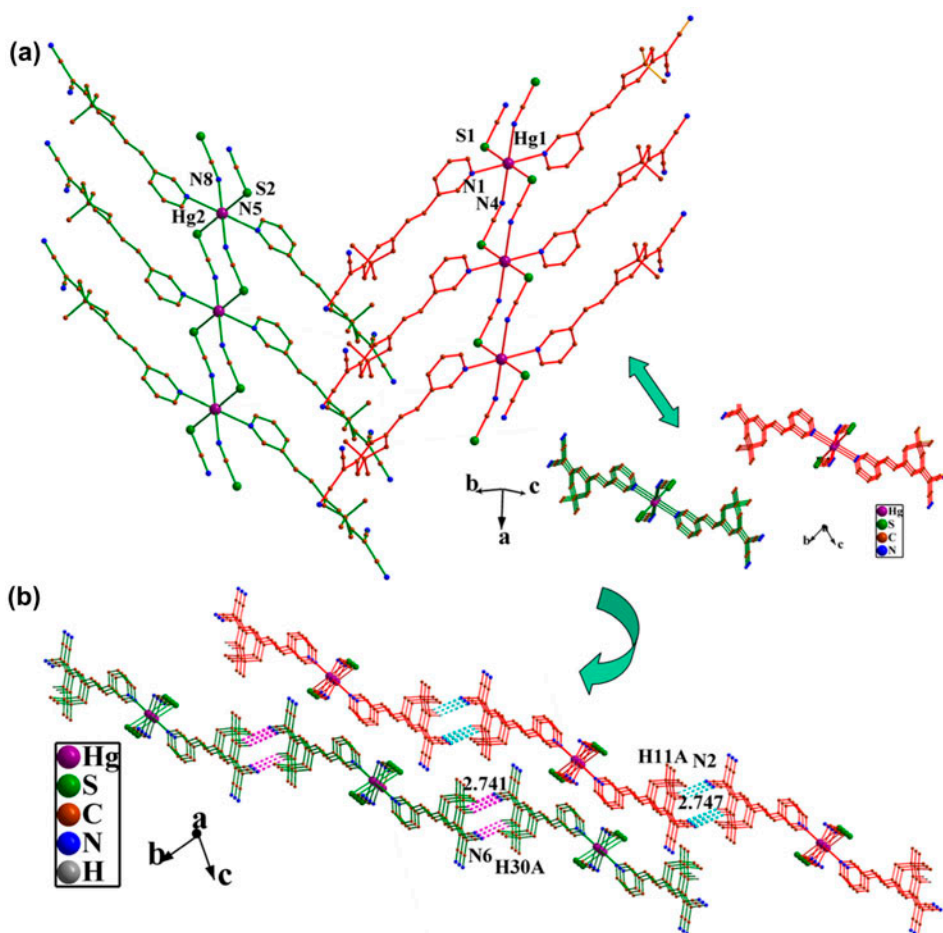


Figure 2. (a) A pair of parallel 1-D chains of **2**. (b) The double parallel 2-D sheets of **2** formed by C–H...N hydrogen bonding interactions. Dotted lines represent the hydrogen bonding interactions. Hydrogen not participating in hydrogen bonding are omitted for clarity.

(30)–H(30A)···N(6) interactions with distance of 2.747 and 2.741 Å, respectively, to form two 2-D sheets. The 2-D sheets are further stacked through C(20)–H(20)··· π and C(1)–H(1)··· π interactions (the distance of H(20)··· π and H(1)··· π is 3.397 and 3.248 Å, respectively) between two pyridyl rings to generate the 3-D supramolecular structure (figure S1, Supplementary material).

3.2.3. [Hg(L2)($\mu_{1,3}$ -SCN)(SCN)]_n (3**).** Polymer **3** is an isomer of **1**. Single-crystal X-ray diffraction analysis reveals that **3** crystallizes in the triclinic system, space group *P* $\bar{1}$. As shown in figure 3(a), **3** features a 1-D polymeric array of [Hg(L2)($\mu_{1,3}$ -SCN)(SCN)]_n. The asymmetric unit of **3** also contains two crystallographically and conformationally independent units in the asymmetric unit cell, and the two independent units extend to form parallel 1-D chains along the *a*-axis. An unusual feature of **3** is the presence of two types of

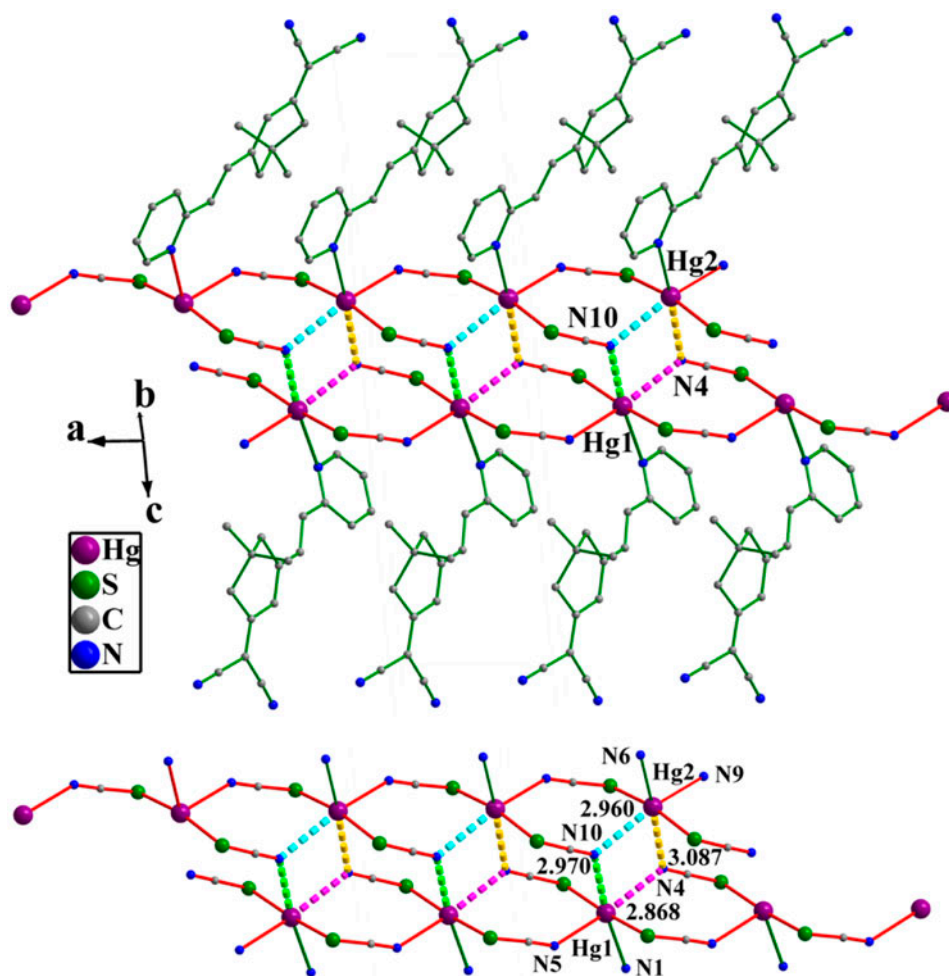


Figure 3. The 1-D structure of **3**. Dotted lines represent the weak interactions. Hydrogen are omitted for clarity.

thiocyanates in the 1-D structure: one is a S-terminal ligand, and the other has a $\mu_{1,3}$ -SCN bridge. In each chain, the neighboring mercury(II) centers are bridged by $\mu_{1,3}$ -SCN groups. The neighboring distances of Hg(1)···Hg(1) and Hg(2)···Hg(2) are 5.905 Å. The S–C–N bond angles are 176.5(5) and 177.4(5)°, indicating that the SCN[−] groups are linear.

Both Hg centers are four-coordinate by two nitrogen donors from **L2** and a bridging thiocyanate, two sulfurs from a bridging thiocyanate, and a S-terminal thiocyanate. As shown in table S1, Hg–N and Hg–S bond lengths are within the normal range [17–20]. Hg(1) and Hg(2) ions weakly interact with N(4) and N(10). Thus, the two parallel chains are linked by Hg(1)···N(10) and Hg(2)···N(4) to form a 1-D double chain (figure 3(a)). The two nearest separations of Hg(1)···Hg(2) are 4.326 Å. The distances of Hg(1)···N(10), Hg(1)···N(4), Hg(2)···N(10), and Hg(2)···N(4) (2.970, 2.868, 2.960, and 3.087 Å, respectively) are shorter than the sum of the van der Waals radii of N (1.55 Å) [19] and Hg (1.73 Å) [21–23].

In the crystal structure of **3**, uncoordinated $-\text{C}\equiv\text{N}$ contributes to higher dimensional supramolecular structures through $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonding interactions. Parallel neighboring double chains (figure 4) are connected by $\text{C}(27)-\text{H}(27)\cdots\text{N}(2)$ and $\text{C}(7)-\text{H}(7)\cdots\text{N}(8)$ hydrogen bonding interactions of 2.618 and 2.556 Å, respectively, to form a 2-D supramolecular structure. The 2-D sheets are further linked by $\text{C}(22)-\text{H}(22)\cdots\text{N}(3)$ and $\text{C}(31\text{B})-\text{H}(31\text{B})\cdots\text{N}(7)$ interactions at 2.618 and 2.556 Å, respectively, to generate the 3-D supramolecular structure (figure 5).

Polymers **1–3** all exhibit 1-D supramolecular structures, in which mercury(II) ions are bridged by $\mu_{1,3}$ -SCN. However, significant differences exist in the three polymers. In **1**, the thiocyanates have $\mu_{1,3}$ coordination and Hg(II) is five-coordinate, as one **L1** coordinates to each Hg(II). As far as **2** is concerned, thiocyanates have the same coordination as **1**. However, Hg(II) centers are six-coordinate and two **L1** coordinate, which is different from **1**. An unusual feature of **3** is the presence of two types of thiocyanates, one S-terminal and the other $\mu_{1,3}$. The Hg(II) centers are four-coordinate and one **L2** coordinates in each unit. Higher dimensional structures of **1–3** are formed through different weak interactions.

3.3. Luminescent properties and thermal stabilities

For potential applications as luminescent materials, luminescences of **1–3** have been investigated in the solid state at room temperature. The polymers were all excited at 380 nm. In measurements of emission and excitation spectra, the pass width is 10 nm for all polymers. Figure 6 presents the emission spectra of **1–3**. **L1** and **L2**, which have been reported in our previous work, exhibit emission maxima at 516 and 511 nm, respectively, which are assigned to the $\pi-\pi^*$ transition [14]. Compared to those of **L1** or **L2**, the emission spectra maxima of **1–3** appear at 518, 519 and 521 nm, respectively, assigned to intraligand $\pi-\pi^*$ transitions because of the resemblance of the emission spectra in comparison with the free ligands. The red shift of **3** compared to the free ligand may arise from coordination.

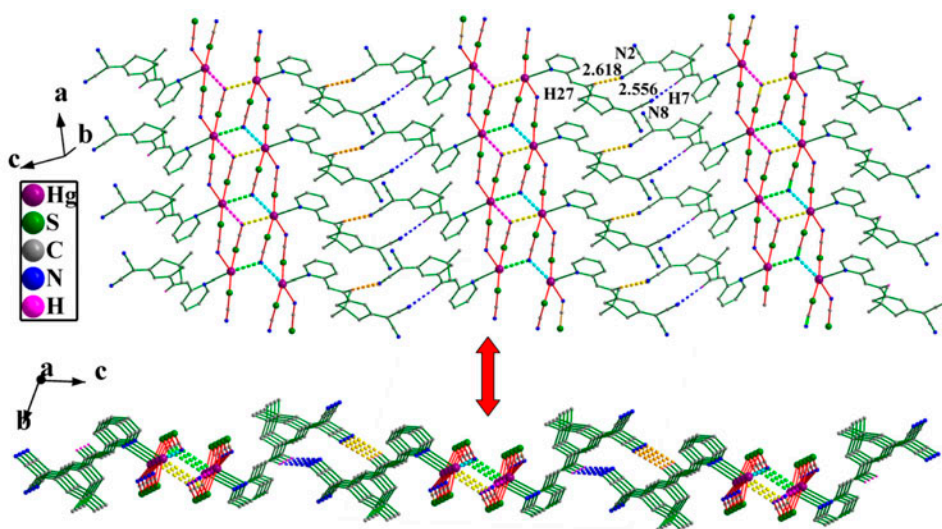


Figure 4. The 2-D structure of **3**. The hydrogen not participating in hydrogen bonding are omitted for clarity.

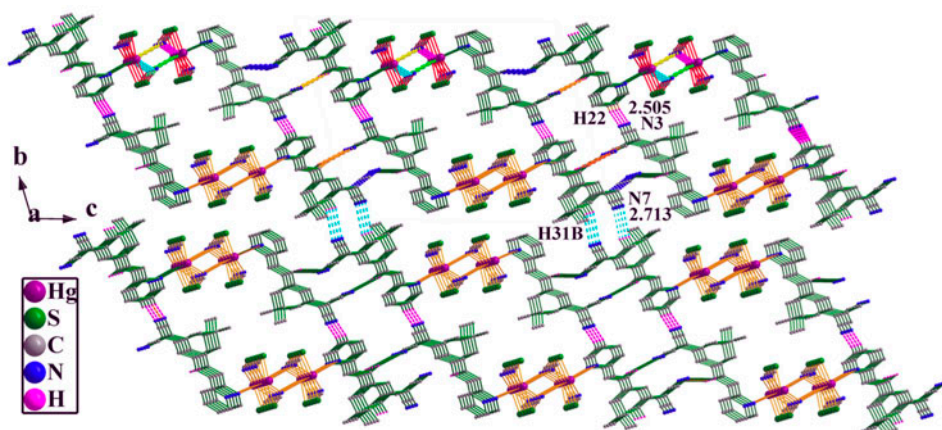


Figure 5. The 3-D structure of **3** formed by C–H···N hydrogen bonding interactions. The dotted lines represent the hydrogen bonding interactions. Hydrogen not participating in hydrogen bonding are omitted for clarity.

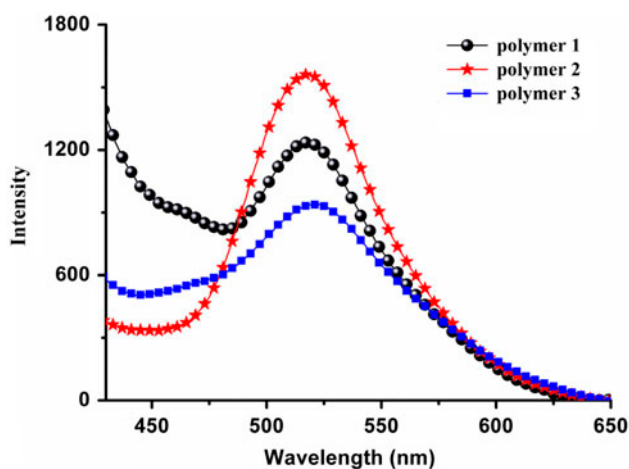


Figure 6. Solid-state emission spectra of **1–3** at room temperature. In measurements of emission and excitation spectra, the pass width is 10 nm.

Incorporation of metal ion may increase the planarity and conformational rigidity, reducing loss of energy via intramolecular vibrational and rotational motions [24]. The best plane and conjugation of the ligand in the polymer may result in a smaller HOMO-LUMO gap [25].

Thermal stabilities of the title polymers were determined by TG. The TG curves exhibit that **1–3** are stable to their decomposition temperatures of 176, 166, and 180 °C, respectively (figure S2). The sharp decomposition processes of **1–3** take place at 176–401, 166–439, and 180–490 °C, respectively, corresponding to loss of the ligands.

4. Conclusion

Two ligands containing pyridyl and dicyanoisophorone groups, 2-{5,5-dimethyl-3-[2-(pyridin-3-yl)-ethenyl]cyclohex-2-enylidene}propanedinitrile (**L1**) and 2-{5,5-dimethyl-3-[2-(pyridin-2-yl)-ethenyl]cyclohex-2-enylidene}propanedinitrile (**L2**), have been used to construct three thiocyanate-bridged Hg(II) coordination polymers. Single-crystal X-ray structures indicate that $\mu_{1,3}$ -SCN appears in the three mercury(II) thiocyanate polymers, rarely reported in a series of mercury(II) thiocyanate complexes. The $\mu_{1,3}$ -SCN and different weak interactions play key roles in the formation of different supramolecular structures. The solid-state luminescent properties and thermal stabilities of **1–3** have been investigated.

Supplementary material

CCDC 908653, 919425, and 908652 contain the supplementary crystallographic data for **1**, **2**, and **3**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version <http://dx.doi.org/10.1080/00958972.2013.851383>.

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